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Highly nitrated cyclopropanes as new high energy materials: DFT calculations on the properties of $C_3H_{6-n}(NO_2)_n$ (n = 3–6)

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1. Introduction

The search for new high energy density materials is an ongoing process [1a,b]. Many known high energy materials share some similar bonding characteristics, among them small rings and high nitrogen content. It is these two characteristics that we have tried to exploit in the past in studies of three-membered rings containing nitrogen atoms [2], boron atoms [3], or both [4].

The enthalpy of combustion of cyclopropane, C_3H_6, is -2091.3 kJ mol^{-1}, or about -49.8 kJ g^{-1} [5]. The idea of adding oxidizing groups like nitro (NO_2) groups to the cyclopropane backbone is not new: the first derivative of a nitrocyclopropane was announced in 1919 by Kohler and Engelbrecht [6], who isolated 1-benzoyl-2-phenyl-3-nitrocyclopropane. The first apparent synthesis of the parent compound nitrocyclopropane, $C_3H_5NO_2$, was reported in 1953 by Haas and Schechter [7], who mixed cyclopropane vapors with N_2O_4 at 420–455 °C or with HNO_3 vapors at 390–410 °C for several second in a spiral Pyrex tube, then immersed the tube in an ice water bath and collected and purified the resulting liquid. Nitrocyclopropane was isolated in 4–15% yield, and the researchers measured a boiling point of 65–67 °C and a density of 1.136 g mL^{-1}. The researchers noted that nitrocyclopropane was relatively unreactive towards oxidation, bromination, or the presence of alkalies.

Although there have been several studies on the energetic properties of nitrocyclopropane, they focus mostly on how the nitro group affects the strain energy of the cyclopropane moiety [8] or on the C–NO_2 bond energy [9]. However, nitrocyclopropane has only recently been included in studies of high energy density materials as a possible fuel or explosive [10,11], but largely as parts of larger molecules. However, Liu et al. [10] did include nitrocyclopropane in their list of energetic nitro compounds, so the idea of nitrocyclopropane as high energy materials is not completely new.

Dinitrocyclopropane was first prepared by Wade, Dailey, and Carroll in 1987 [12] by oxidative cyclization of 1,3-dinitropropane. Only the *trans* isomer was isolated. They also performed Hartree–Fock calculations and found good agreement with the X-ray structure of the molecule. However, they did not report on any thermochemical analyses. Bowyer and Evans reported on cyclic voltammetry studies of several dinitrocycloalkanes, including 1,2-dinitrocyclopropane, but stated that they were "not able to interpret the voltammograms quantitatively" and did not comment on results for this substance further [13]. Sorescu, Rice, and Thompson included dinitrocyclopropane in a series of nitroalkanes in a simulation to develop an intermolecular potential model for these compounds [14], but the focus was solid-state properties rather than energetics of reaction. As final evidence for considering that dinitrocyclopropane may have some high energy density applications, Sullivan, Wade, and Turetsky were recently granted a patent (US Pat. # 6,007,648) for a new liquid explosive containing dinitrocyclopropane as one component [15].

Although there are no published studies on cyclopropane with larger numbers of nitro groups, it is feasible that such compounds can be synthesized, perhaps by nitronium hextfluorophosphate as outlined by Olah et al. [16]. As such, here we report on the structures, vibrational spectra, and thermochemical properties of

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cyclopropane rings having three to six nitro groups. Studies like this are useful because they can provide justification for synthetic efforts towards such molecules.

2. Computational details

All calculations were performed using Gaussian03 [17] on a desktop personal computer. The calculational method used was the density functional theoretical method using Becke's 3-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (abbreviated B3LYP) [18,19] along with the standard Gaussian basis set labeled 6-31G(d,p) [20]. Minimum energy geometries were determined for all target molecules using standard options, and minima were verified as having no imaginary vibrational frequencies, which were visualized using the GaussView program [21].

After geometry optimization, enthalpies of formation were determined using the following reaction:

$$C_3H_6(g) + n/2\ N_2O_4(g) \rightarrow C_3H_{6-n}(NO_2)_n(g) + n/2\ H_2(g)$$

The electronic and thermal energies of C_3H_6, N_2O_4, and H_2 were also calculated using the same methods, and the enthalpy change of the above reaction was determined using Hess' law. Then, setting the enthalpy change as determined to the enthalpy of formation of products minus the enthalpy of formation of the reactants as using the known ΔH_f values from the NIST Chemistry Webbook website [22], the enthalpy of formation of the various nitrocyclopropanes were calculated. Enthalpies of combustion or decomposition could then be determined for each nitrocyclopropane. Vibrational spectra were visualized using the SWizard program [23] and confirmed that, with no imaginary vibrational frequencies, the optimized geometries were energy minima. No conformational study of the relative positions of the NO_2 groups was performed.

3. Results and discussion

3.1. Geometries

Fig. 1 shows the optimized geometries of trinitrocyclopropane, tetranitrocyclopropane, pentanitrocyclopropane, and hexanitrocyclopropane, respectively. Table 1 lists representative structural parameters. The table shows that some of the parameters in tetranitrocyclopropane and pentanitrocyclopropane show some variation, which makes sense given that the carbon atoms are not equivalent, having differing numbers of nitro groups on them. There is some variability in the C–C bond distances in trinitrocyclopropane, because one of the nitro groups adopts a position *trans* to the other two. Table 1 shows that the C–N bond distance increases noticeably, by over 0.050 Å, as the nitration level of the ring increases. Curiously, the N–C–N bond angle decreases with increasing nitro content. Fig. 1 shows that when there are two nitro groups on a carbon atom, the NO_2 groups orient themselves so that they look like they are crossing when viewed from above.

3.2. Vibrational spectra

Fig. 2 shows the vibrational spectra of the four nitrocyclopropanes. All of the spectra are dominated by NO_2 bending and stretching modes, and the domination gets greater as the NO_2 content increases. The low-frequency region is rather messy to start, with a large number of weak absorptions due to the lack of symmetry of trinitrocyclopropane. However, for hexanitrocyclopropane, the vibrational spectrum is rather clean as degeneracy or near-degeneracy causes many absorptions to merge into a single peak. Indeed, the peak around 1730 cm^{-1} for hexanitrocyclopropane is actually composed of six absorptions, five of which have calculated absolute intensities of greater than 240 km mol^{-1}, while

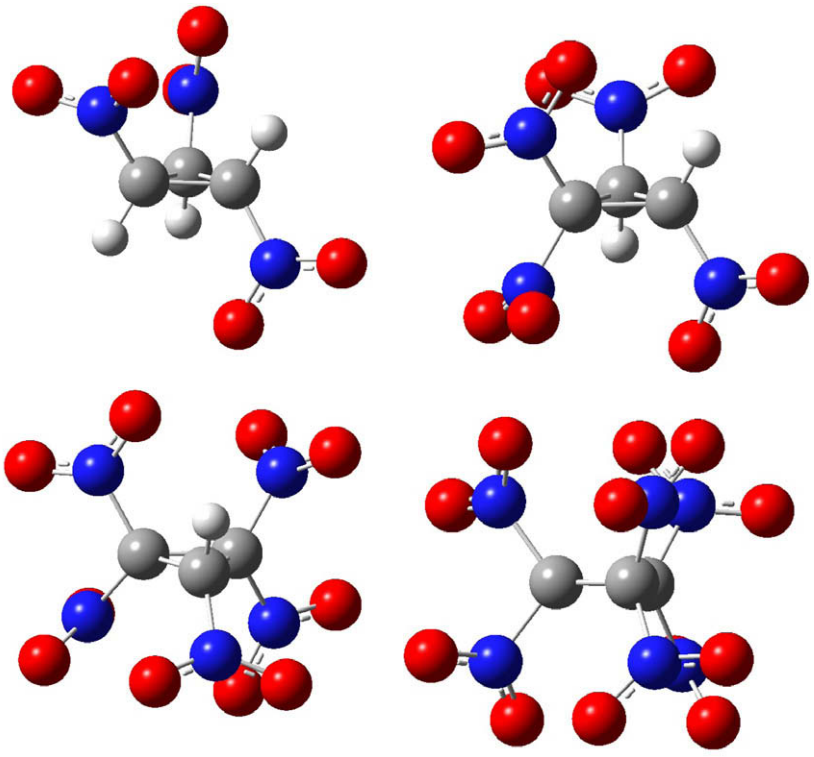

Fig. 1. Optimized geometries of trinitrocyclopropane (upper left), tetranitrocyclopropane (upper right), pentanitrocyclopropane (lower left), and hexanitrocyclopropane (lower right).

Table 1
Representative structural parameters of minimum-energy nitrocyclopropanes (r in Å, δ and α in degrees).

Molecule	Trinitrocyclopropane	Tetranitrocyclopropane	Pentanitrocyclopropane	Hexanitrocyclopropane
r(C–C)	1.498	1.490, 1.514	1.497, 1.509	1.496
r(C–H)	1.082	1.084	1.088	–
r(C–N)	1.481	1.486, 1.502	1.506–1.522	1.532
r(N–O)	1.222	1.221	1.213, 1.223	1.215
δ(C–C–C)	59.0, 61.0	59.6, 61.1	59.3, 60.8	60.0
δ(C–C–H)	118.6	120.0	114.3	–
δ(C–C–N)	120.1	119.9	115.5–125.6	122.0
δ(O–N–O)	126.9	127.9	128.0–128.8	129.2
δ(H–C–N)	112.7	113.3	110.1	–
δ(N–C–N)	–	111.3	109.2	106.6
α(C–C–C–H)	108.1	110.6	105.1	–
α(C–C–C–N)	104.9	109.3	110.2, 115.6	109.1
α(C–C–N–O)	37.0	44.1	52.0	15.0

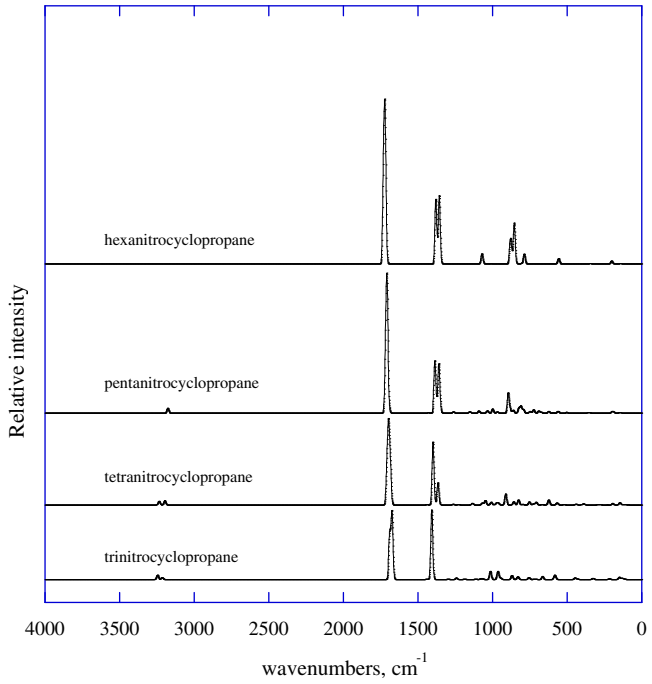

Fig. 2. Calculated (unscaled) vibrational absorption spectra for the nitrocyclopropanes.

the doublet centered about 1370 cm^{-1} encompasses five absorptions between 1345 and 1380 cm^{-1}, with three of them having absolute intensities of 190 km mol^{-1} or greater. Of the 57 normal vibrations in hexanitrocyclopropane, 17 of them are calculated as having an absolute intensity of <0.01 km mol^{-1}, and many of these (if not more) would be exactly zero if the geometry of the molecule had been constrained to have exact 3-fold symmetry.

Persons wishing to study the normal modes of vibration are invited to contact the authors for copies of the output files for their own visualization.

3.3. Enthalpies of reaction

Table 2 lists the calculated enthalpies of formation and the resulting enthalpies of combustion and decomposition. The enthalpies of formation are all positive, and get more so as the nitro content of the molecule increases. This is consistent with an increased steric interference as bulky nitro groups start amassing on the second side of the cyclopropane backbone.

The reaction used for the combustion reaction of trinitrocyclopropane was

Table 2
Enthalpies of reaction for the nitrocyclopropanes (in kJ mol^{-1} unless otherwise stated).

	ΔH_f	ΔH_{comb}	ΔH_{comb}, kJ g^{-1}	ΔH_{decomp}	ΔH_{decomp}, kJ g^{-1}
Trinitrocyclopropane	73.8	−1683.1	−9.51	−1258.6	−7.11
Tetranitrocyclopropane	114.9	–	–	−1611.3	−8.76
Pentanitrocyclopropane	244.1	–	–	−1567.6	−5.87
Hexanitrocyclopropane	338.2	–	–	−1518.7	−4.87

$$3/4\ O_2(g) + C_3H_3N_3O_6(g) \rightarrow 3/2\ H_2O(\ell) + 3CO_2(g) + 3/2\ N_2(g)$$

Only trinitrocyclopropane has an enthalpy of combustion different from its enthalpy of decomposition, as its negative oxygen balance (OB%) of −13.6% [23] indicates that it does not contain enough oxygen in its formula to completely oxidize the other atoms in the molecule. The reaction used to determine the decomposition reaction of trinitrocyclopropane is

$$C_3H_3N_3O_6(g) \rightarrow 3/2\ CO_2(g) + 3/2\ CO(g) + 3/2\ H_2O(\ell) + 3/2\ N_2(g)$$

The formation of CO as a product is consistent with the Kistiakowsky–Wilson rules for decomposition [24]. For trinitrocyclopropane, the results show that the combustion reaction generates only about 33% larger energy per unit mass than the decomposition, and both values are substantially higher than the specific enthalpies of decomposition of trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), which are listed as 4.25 and 5.04 kJ g^{-1}, respectively [24].

At +7.2%, +21.0%, and +30.8%, the OB% of tetranitrocyclopropane, pentanitrocyclopropane, and hexanitrocyclopropane are high enough that there is enough oxygen to completely oxidize the C and H atoms in each formula. The general reaction used for the decompositions of these compounds is

$$C_3H_{6-n}(NO_2)_n(g) \rightarrow 3CO_2(g) + \left(\frac{6-n}{2}\right)H_2O(\ell) + \left(\frac{5n-18}{4}\right)O_2(g)$$

where n is the number of nitro groups on the cyclopropane ring.

The trend in ΔH_{decomp} versus nitro content is very interesting: at four nitro groups on the cyclopropane ring, the enthalpy of decomposition is at a maximum, then it decreases – both per unit mole and per unit gram – as additional nitro groups are attached to the cyclopropane backbone. This decrease is the combination of two trends: the increasing enthalpy of formation of the nitrocyclopropane and the decreasing amount of water formed as n increases. What we find here is similar to what has been found with other polynitro compounds: although the enthalpies of formation increase with nitro content, the enthalpy of decomposition does not rise fast enough to keep up with the increase in mass of

the compound. Hence, while the enthalpy of formation increases with increasing nitro content, the enthalpy change *per unit gram* upon decomposition decreases. Ultimately, hexanitrocyclopropane is predicted to have an only slightly higher specific enthalpy of decomposition than trinitrotoluene.

Whether or not polynitrocyclopropanes would make effective high energy materials depends on additional properties, like condensed-phase density and velocity of detonation. Nitrocyclopropane was reported [7] to have a density of 1.136 g mL^{-1}, which is not high for a high energy material. There is no report of a density for dinitrocyclopropane. If we compare the densities of various nitrocubanes, however, we might hazard an education guess on the possible densities of higher nitrocyclopropanes. Cubane has a reported density of 1.29 g mL^{-1} [25], nitrocubane has a density of 1.453 g mL^{-1} [26], tetranitrocubane has a density of 1.814 g mL^{-1} [27], while heptanitrocubane and octanitrocubane have densities of 2.028 and *ca.* 2.2 g mL^{-1}, respectively [27]. Thus, we see a ~13% increase in density when adding a single nitro group and a ~71% increase in density when the polycyclic hydrocarbon is fully nitrated. Liquid cyclopropane has an extrapolated density of 0.743 g mL^{-1} [28]; a 71% increase in mass would bring the estimated density of hexanitrocyclopropane to 1.27 g mL^{-1}, which is still rather low for a good high density material. However, from an energy content perspective, polynitrocyclopropanes are predicted to have at least as much enthalpy of decomposition per unit grams as some currently-known high energy materials. There is also the attendant issue of synthesis, which we will leave to the synthesist.

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